Atmos. Chem. Phys. Discuss., 9, C8353–C8368, 2009
www.atmos-chem-phys-discuss.net/9/C8353/2009/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Background ozone over Canada and the United States" *by* E. Chan and R. J. Vet

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Received and published: 14 December 2009

Authors' responses to reviewer #1 are as follows:

Main concerns:

1. The 95th percentile directly links to a single effect. Predominately for remote locations, this effect is associated with long-range transport. The mean/median however, is the end result of a number of effects, for example, the effects due to long-range transport contributing to high ozone levels, and dry depositions and NO scavenging removing ozone. Nonetheless, the authors also attempted to use the "lowest median" but the resulting clusters of trajectories would for some sites be associated with flows originated within the continent passing over high emission NOx and NMHC source areas.

The transports were also relatively close to the surface. The ozone levels during the wintertime for the "lowest median" trajectory cluster were more affected by NO scavenging and/or depositions. This is also evidenced in Fig. 5b that cluster 4 could have been selected using the "lowest median" criterion. However, the box-and-whiskers in the winter months indicate that the ozone level associated with this cluster is lower than that associated with cluster 6, which was selected using the "lowest 95th percentile" criterion. The 95th-percentile criterion used in this study is robust in a sense that the screened out ozone data have the least regional-scale photochemical influences during the summer and guarantee the least influences due to various removal processes particularly during the winter. The lowest medians will not guarantee such perfect removal on the high end and low end of the ozone distribution at a given site.

The cleanest cluster was then objectively and systematically chosen using the method for all 97 non-urban ozone sites. It is highly reproducible. As opposed to using wind direction for instance, the choice of the width of a clean sector and/or wind speed can also be rather subjective. The use of local wind information cannot avoid cases where the trajectory starts out over the polluted region, then turns enough that it reaches the measurement site from the clean sector (Carslaw 2005; Simmonds et al. 2004).

It is even more problematic to apply to a broad suite of sampling locations. The idea in this study was to systematically remove as much regional-scale photochemically formed ozone as possible through the use of 10-year of trajectory climatology at all sites considered in this study across Canada and the US. As shown in this study, the background of ozone represented by the cleanest air mass cluster can origin in many pristine locations, not necessarily associated with westerly oceanic inflows.

2. This is exactly the reason why PCA was done prior to dataset screening based on trajectory analysis. The idea was first to reveal ozone variability due to the combination of anthropogenic and/or natural influences over a broad spatial extent. Then comparison can be made from north to south, from west to east and from low to high attitude to investigate temporal variability over space (of lack thereof) as opposed to have one

or two large regions. The trajectory analysis is effective in separating background and polluted conditions as shown in PC1, PC5, PC6, PC8, PC10, PC11 (low altitude regions) and PC7 and PC9 (high altitude regions) in Fig 8a and 8b. The coherent trends within above regions have clearly been demonstrated the effectiveness of the trajectory analysis method. However, even for non-urban sites, the regional/local influences for the rest of the regions are simply too large to screen out the "background" condition by any means.

Additionally, the general rule of thumb for obtaining reliable and recognizable PCA pattern is to have at least the number of "complete" observations equal to five to ten times the number of variables (number of sites) to have a moderately stable result (MacCallum et al., 1999; Costello and Osborne, 2005; Garson, 2008). In this case 97 x 10 = 970 complete observation records for every season is required. For a single site, this is approx. 730 observations available. This is calculated by 4 six-hly averages x 365 days x 10 years / 4 seasons x (approx 10 – 20%) of "background" data = 730. However, a complete observational record in this sense for PCA represents data available for all 97 sites at the same time step. We calculated that there was not enough complete observational records to worth attempting Reviewer #1's suggestion.

References:

MacCallum, R. C., Widaman, K. F., Zhang, S. & Hong, S.: Sample size in factor analysis, Psychological Methods, 4, 84-99, 1999.

Costello, A. B. & Osborne, J. W.: Best practices in exploratory factor analysis: four recommendations for getting the most from your analysis, Practical Assessment, Research & Evaluation, 10, (7), 2005.

Garson, D. G., Factor Analysis: Statnotes, North Carolina State University Public Administration Program, 2008.

3. The authors do find the suggestion from the reviewer #1 very helpful. The definition

of "background" through observational study should be carefully phrased.

We would use the definition with a slight modification from Parrish et al., 2009. We would add to the manuscript: "The term background ozone is qualitatively defined as ozone mixing ratios measured at a given site in the absence of strong regional and local influences (similar to what Parrish et al., 2009 defined). To contrast with the definition through a chemical transport model by Fiore et al. (2003), in which they defined background that "consists of the combination of naturally and anthropogenically produced ozone from outside of the US, plus naturally formed ozone within the US". The two definitions are very different in concept and therefore, the numerical values are not directly comparable. It is difficult to turn off all ozone precursor emissions from all regional and local sources from the observational perspective, whereas, it is equivalently difficult to isolate clean background air flows from a modeling framework. Much collaboration between the observational and modeling communities is required to reconcile the difference to improve the ability for observational trend attribution and model evaluation."

Specific comments: Abstract has been rewritten as follows. However, to expand on the decadal trends across seasons and regions, it was not possible to have less than 250 words.

"Planetary boundary layer (PBL) ozone temporal variations were investigated on diurnal, seasonal and decadal scales using ground-level in situ observations in various regions across Canada and the United States for the period 1997–2006. Background ozone is difficult to quantify and define through observations. In light of the importance of its estimates for achievable policy targets, evaluation of health impacts and relationship with climate, background ozone mixing ratios were estimated. Principal Component Analyses (PCA) were performed using 97 non-urban ozone sites for each season to define contiguous regions. Backward air parcel trajectories were used to systematically select the cleanest background air cluster associated with the lowest May–September 95th percentile for each site. Decadal ozone trends were estimated by season for each PCA-derived region using a generalized linear mixed model (GLMM).

Background ozone mixing ratios were variable geographically and seasonally. For example, the mixing ratios annually ranged from 21 to 38, and 23 to 38 ppb for the continental Eastern Canada and Eastern US. The Pacific and Atlantic coastal regions typically had relatively low background levels ranging from 14 to 24, and 17 to 36 ppb, respectively. On the decadal scale, increasing trends were observed along the Pacific coast of Canada and the US in all seasons, although the trends in California were not statistically significant. The statistically significant, temperature-adjusted ozone decadal trends in British Columbia, Canada increased at a rate of 0.28±0.26, 0.72±0.55, and 0.93±0.41 ppb/a in MAM, JJA, and DJF, respectively. In the Atlantic coastal zone, the trends were positive (but significantly only in MAM), except in the DJF when the trend was negative (but not significant). Background ozone decadal changes are shown to be masked by the much stronger regional signals in areas that have seen substantial reductions of ozone precursors since the early 2000s."

Section 1.2 has been rewritten as follows. "As reported by the Intergovernmental Panel on Climate Change (IPCC, 2001, 2007), tropospheric ozone is the third most important anthropogenic greenhouse gas (GHG), following CO2 and CH4. IPCC studies have shown that tropospheric ozone is expected to continue rising (Ehhalt et al., 2001) due to the increase in economic activity of many developing countries as they consume more fossil fuel. In short, as the global temperature continues to rise, more favourable conditions for ozone formation will occur (e.g., increased isoprene availability, soil-NOx emissions (Zeng et al., 2008), wildfires (Jaffe et al., 2008)). Since tropospheric ozone is expected to have a direct positive radiative forcing on climate (Ehhalt et al., 2001; Ramaswamy et al., 2001), this possible feedback mechanism may warm the earth's atmosphere further in the future. However, it remains unclear on whether tropospheric ozone will increase or decrease in a warmer climate as increased water vapor can shorten the ozone atmospheric lifetime (Johnson et al., JGR, 1999; Gauss et al., ACP, 2006; Stevenson et al., JGR, 2006; Wild, ACP, 2007). Further work is needed to

provide constraints on the response of ozone to temperature increases for a more accurate model prediction of effect of climate change on air quality (Ito et al., 2009). Modeling studies have already shown that there is a strong inter-relationship between tropospheric ozone, GHGs, climate and regional air quality (West et al., 2007; Fiore et al., 2008). Therefore, the quantification of different temporal variations of ozone in the entire troposphere through observations is needed in current atmospheric research. A clear distinction should be made here that it was the ground-level ozone (from 2 m to 3 km in altitude) considered in this study and tropospheric ozone (extends to between 10 and 20 km above ground) which is relevant for climate forcing."

References:

Johnson, C. E., Collins, W. J., Stevenson, D. S. and Derwent, R. G.: Relative roles of climate and emissions changes on future tropospheric oxidant concentrations, J. Geophys. Res., 104(D15), 18,631–18, 645, 1999.

Gauss, M., Myhre, G., Isaksen, I. S. A., et al.: Radiative forcing since preindustrial times due to ozone change in the troposphere and the lower stratosphere, Atmos. Chem. Phys., 6, 575-599, 2006.

Stevenson, D. S., Dentener, F. J., Schultz, M. G., et al.: Multimodel ensemble simulations of present-day and near-future tropospheric ozone, J. Geophys. Res., 111, D08301, doi:10.1029/2005JD006338, 2008.

Ito, A., Sillman, S., and Penner, J. E.: Global chemical transport model study of ozone response to changes in chemical kinetics and biogenic volatile organic compounds emissions due to increasing temperatures: Sensitivities to isoprene nitrate chemistry and grid resolution, J. Geophys. Res., 114, D09301, doi:10.1029/2008JD011254, 2009.

Section 1.3. The background definition has been re-written.

Section 1.6 + 1.7. We have combined sections 1.6 and 1.7 and added the citations according to reviewer #1's suggestion.

Section 1.8. L24-26 have been removed to reflect previous work (those studies cited, as well as Parrish et al., 2009; the Jaffe et al studies cited; Lin et al., 2000; Wang et al., 2009) that addresses seasonal and day-to-day variability. Further, several studies referenced examined background ozone across the entire United States: e.g., Lin et al., 2000; Fiore et al., 2002 and 2003; Wang et al 2009. Lefohn et al, 2001 (Journal of Geophysical Research-Atmospheres) have been included.

Section 2. The reason of using daily values was to avoid local influences (as explained in 21117 L27) and be readily comparable with other ozone trends where daily values were modeled (Holland et al., 1999; Duenas et al., 2002; Vingarzan and Taylor, 2003; Tarasova and Karpetchko, 2003; and many others). The daily ozone values of ozone were found to be best explained by daily temperature values in terms of meteorological influences. Six-hour averages were used for the seasonal variations because we would like to show the full variability for every month throughout the year.

Importance of temperature on trends in the background ozone or ozone in general has been studied by various groups. Temperature is the best proxy to account for meteorological influences (sunlight, humidity, mixing, etc.) in ozone long-term changes (Bloomfield et al., 1996; Chan, 2009, and many others), particularly during the summertime as shown in this study in Table 2. The expected influence of temperature on trends in the background ozone or tropospheric ozone in general is positive trend enhancement.

References:

Bloomfield, P., Royle, J. A., Steinberg, L. J. and Qing, Y.: Accounting for meteorological effects in measuring urban ozone levels and trends, Atmos. Environ., 30, 3067– 3077, doi:10.1016/1352-2310(95)00347-9, 1996.

Holland, D., Principe, P. P., and Vorburger, L.: Rural Ozone: Trends and Exceedances at CASTNet Sites, Environ. Sci. & Tech., 33 (1), 43-48, 1999.

Duenas, C., Fernandez, M. C., Canete S. et al.: Assessment of ozone variations and meteorological effects in an urban area in the Mediterranean Coast, The Sci. of The Total Environ., Volume 299, Issues 1-3, 1 November 2002, Pages 97-113, ISSN 0048-9697, DOI: 10.1016/S0048-9697(02)00251-6, 2002.

Vingarzan, R., Taylor, B.: Trend analysis of ground level ozone in the greater Vancouver/Fraser Valley area of British Columbia, Atmo. Environ., Volume 37, Issue 16, May 2003, Pages 2159-2171, ISSN 1352-2310, DOI: 10.1016/S1352-2310(03)00158-4, 2003.

Tarasova, O. A. and Karpetchko, A. Yu.: Accounting for local meteorological effects in the ozone time-series of Lovozero (Kola Peninsula), Atmos. Chem. Phys., 3, 941-949, 2003.

Chan, E.: Regional ground-level ozone trends in the context of meteorological influences across Canada and the eastern United States from 1997 to 2006, J. Geophys. Res., 114, D05301, doi:10.1029/2008JD010090, 2009.

The Canadian CMC trajectory model is a single particle lagrangian trajectory model comparable to NOAA HYSPLIT. The trajectories are calculated by allowing the parcels to move with the 3-D components of the wind. To answer the reviewer #1's question, no, it does not handle turbulent mixing and convection. In the context of this work, 10-year trajectory climatology was done and the ozone data were sorted into six predominate trajectory clusters. What this study concerned was the recurring regional-scale transport pathways over the 10-year period.

Section 3.2. Certainly, there are many ways to decide the number of components to retain. In PCA, it is always the balance between physical interpretability, manageability of the number of components, the cumulative variance, and more. 75% minimum total variance was chosen because it worked well in many studies that we encountered in the past. To provide a reference here, when researchers use the “cumulative percent of variance accounted for” as the criterion for solving the number-of-components problem, they usually retain enough components so that the cumulative percent of variance accounted for at least 70% (and sometimes 80%) (Hatcher, L, 1994). Setting a fixed percentage total variance for every season allows straightforward comparison in terms of the number of groupings thereby revealing spatial homogeneity across seasons.

Reference:

Hatcher L: A Step-by-Step Approach to Using SAS for Factor Analysis and Structural Equation Modeling. Cary, NC: SAS Press, 1994.

Section 3.5 One can get an idea on the percentage of the data retained for the decadal trend analysis from the statistics shown in Fig 6a. As mentioned in the text, the trend analysis was done on a region basis using GLMM, a multiple-site ensemble approach. In region PC1 for example in JJA, the regional trend was calculated using 18 sites and certainly there were only 4 sites in PC10 in JJA, the western Pacific region, but the uncertainty of the regional trend estimate is reflected in the magnitude of the standard error (+ or -) in Table 2.

These populations of ozone data associated with the background air masses tend to fall roughly in the 1st – 95th percentile range of the overall observed distribution at a given site depending on distance to high density precursor sources. Seasonally, the data associated with the background air masses tend to fall in 1st – 95th, 1st – 90th, 1st – 95th, 1st – 99th for the months of MAM, JJA, SON, and DJF respectively (see attached Fig. 1). This is expected and desirable result since the regional/local-scale influences in terms of ozone formation as well as the low values associated with the removal processes due to e.g. NO titration, deposition are removed.

The physical meaning behind the choices of one-day auto regression represents short-term day-to-day temporal correlations, most probably corresponding to very similar meteorological conditions from yesterday, today and tomorrow. There is no good physical

explanation for the 3-5 year periodicities. These longer term variations allow best fit to the decadal changes. Linear (Jaffe et al., 2003; Parrish et al., 2009) or cubic polynomial (Oltmans et al., 2006) fit used in many trend analysis studies did not have a “perfect” physical explanation behind. We do not believe long-term changes increasing/decreasing monotonically and at the same time we do not want the other higher order polynomial terms (e.g. t2, t3) to confound with the slope (t). It is the trend estimate and uncertainty associated with the slope that is of the most interest.

Section 4.3 It would have been a logical second step to perform, if the two clusters were significantly different from each other all the time (for all months). However, taking Egbert for example, Fig 5b, it shows that clusters 4 and 6 were significantly different in October and November.

Section 4.4 The first paragraph has been moved to Section 4.6. “One of the questions posed in the Introduction was whether domestic ozone precursor emission reduction efforts might still be important in light of the documented (see Sect. 4.6) increase in background ozone. Evidence is provided in the following sections to address this question.”

As pointed out in the text, P21135 L 1-2: “This again implies that these regions are not continentally or hemispherically representative.” And L8-10: “This illustrates the point that because of the slowly-varying nature of the background, the importance of this signal can easily be masked by any major regional-scale ozone signals.” This implies that background and ozone produced from domestic emissions are not easily separable when the regional influences are too strong.

Section 4.5 Because the elevation of the PC9 region is at near the top of the PBL ($\sim$3 km), it is reasonable to suggest that the ozone variations observed at this regions be the upper limit of the sites that are at lower elevations.

Section 4.6 Jaffe et al., EST, 2008 has now been included in the last paragraph.

Reference:

Jaffe, D., Chand, D., Hafner, W., Westerling, A. and Spracklen D.: Influence of Fires on O3 Concentrations in the Western U.S., Environ. Sci. Technol., 42 (16), pp 5885–5891 DOI: 10.1021/es800084k, 2008.

Section 5 Lefohn et al, 2001 and Fiore et al 2003 have been included in this closing section.

Reference:

Lefohn, A. S., Oltmans, S. J., Dann, T. and Singh, H. B.: Present-day variability of background ozone in the lower troposphere, J. Geophys. Res., 106(D9), 9945–9958, 2001.

"……Rather, background ozone, as defined here, varied geographically and seasonally. This conclusion is largely consistent with prior studies in which different methods have been used to investigate background ozone variability (Lefohn et al., 2001; Fiore et al., 2003). However, this study extends beyond prior work."

Technical Comments P21121 L 16-21. A new figure is included for the seasonal variations for six of the regions (see attached Fig. 2) and diurnal variations for the western coastal Canada region (see attached Fig. 3). The black dots show all the six hourly averages. The green dots show the six hourly averages associated with the "background" air flows.

Section 4.2 This section has been clarified. According reviewer #2, we should publish and expand this section in a separate paper. This section serves as an integral part of the paper. In light of the relevant and importance of the PCA-derived regions in terms of grouping ozone sites to be analyzed further subsequently throughout the paper, we feel that it is important to have this section and a moderate amount of details.

Table 1. The ranges represent seasonal ranges of the fitted curve for a given region over 1997-2006. The data used to fit the seasonal curve were from all the sites within

a given region. It is now clear with an illustration (see attached Fig. 2 and Fig. 3) as suggested by the reviewer #1. The diurnal ranges represent the ranges of the fitted curve for a given season for a given region over 1997-2006. It is now clear with an illustration of PC10, the western coastal Canada region.

Table 2. This is for the subset of data selected for the trajectory cluster with the lowest 95th percentile ozone. The caption of the table will be changed to reflect that.

"Decadal background trends modelled by GLMM using daytime (12:00–18:00 LST) average ozone…"

Symbols from original Fig. 1 have been associated with groups in Table 1 to facilitate interpretation in Table 1 captions.

The multi-panels figures e.g. Fig. 6-9 will span over 2/3 of a page in the final ACP version (if accepted) as opposed to less than half a page in ACPD and the editorial office will ensure legibility. In the ACPD version, the authors did not have control over the layout of the figures. Additionally, in the pdf version of the manuscript, the figures can all be zoomed in by 600% without losing pixel resolutions.

Figures 6-9: A consistent layout and flow of the multi-panel figures throughout the paper allows the readers to familiarize and follow easily. Although repeating the same information, the readers do not need to flip back and forth to understand why ozone levels are systematically high in those high elevation regions (particularly important for readers who are not used to the North American topography). Also, ensure the readers that the trajectory clusters we have are representative of clean air vs polluted air by immediately looking at the relative influences through the population density map. Therefore, we propose that no changes are made.

The numbers on the map are explained in P21125 L19-26. This will be referred in the figure captions. The numbers actually have already been explained in the captions.

Multiple lines in Fig. 7-9 are artifacts created by the conversion from our original figures to pdf. The editorial office will ensure that this problem is addressed in the final version.

Figure 10. The shapes were determined by simply joining the site locations defined by seasonal PCA. The numbers correspond to the PCA groupings in Figure 1 (and throughout). The definition of "cleanest air" has been given in the captions.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 21111, 2009.

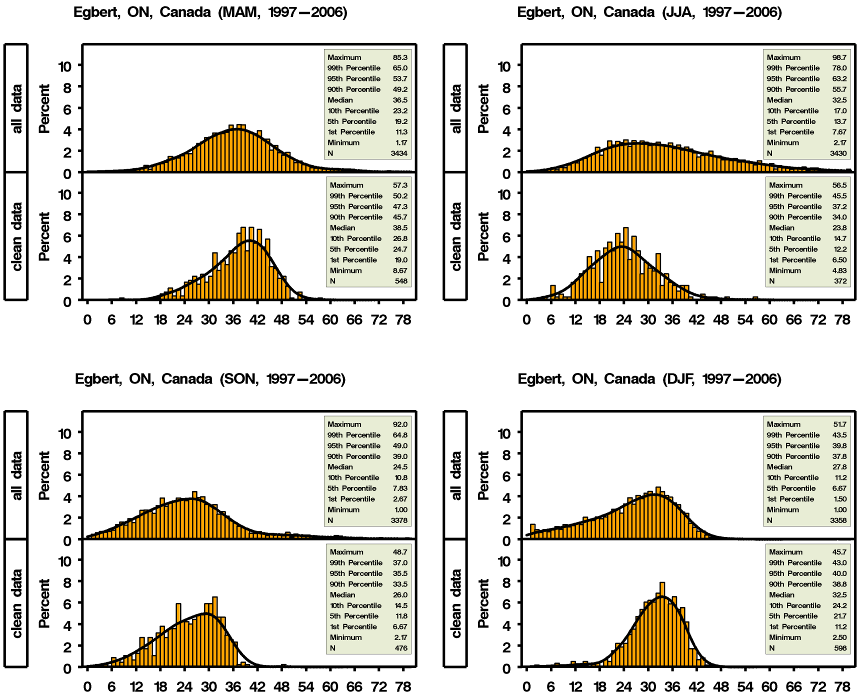

Fig. 1.

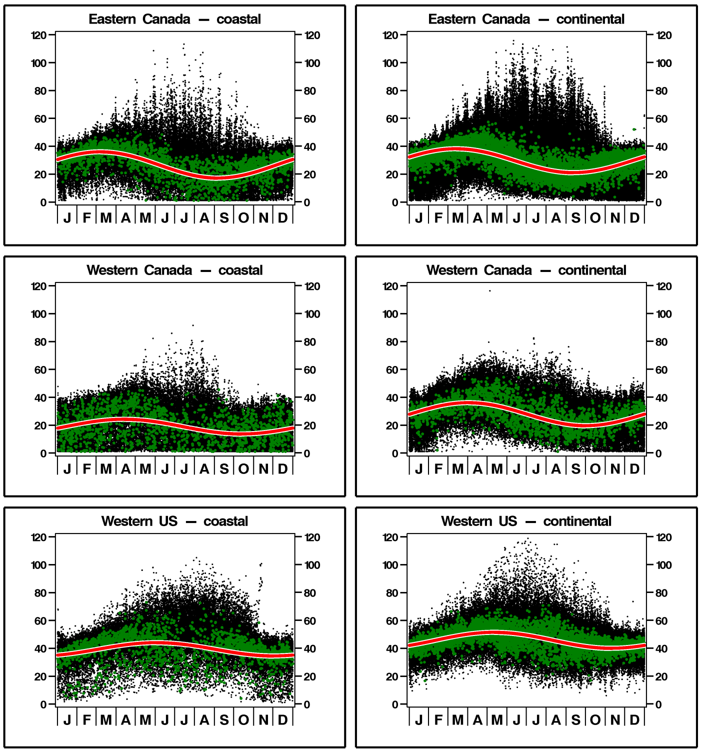
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Fig. 2.

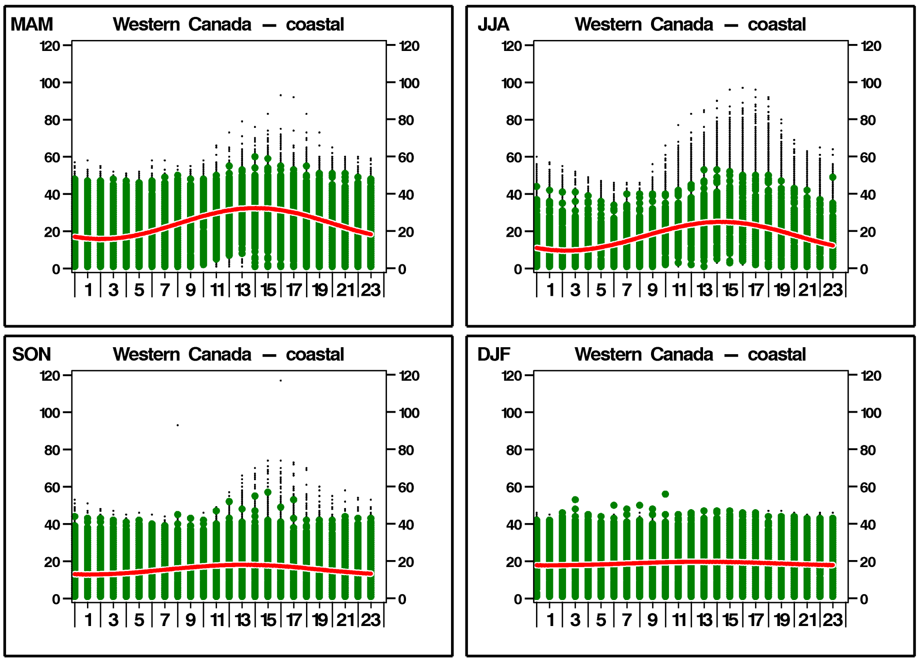
MAM
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Fig. 3.